

PROCESS FOR THE PREPARATION OF AQUEOUS EMULSIONS
OF ADVANTAGEOUSLY MASKED (POLY)ISOCYANATE OILS
AND/OR GUMS AND/OR RESINS AND EMULSIONS OBTAINED.

The present invention relates to a process
5 for the preparation of emulsions of oils and/or gums
and/or resins, which are preferably viscous. Its
subject is more particularly a process for emulsifying
(poly)isocyanates.

Furthermore, diisocyanates, especially
10 alkylene diisocyanates (tolonates) and their
derivatives of biuret type or their trimers are widely
employed in the activity of paints and varnishes.

However, among the problems which remain
unsolved to date, there is one that is particularly
15 acute, namely the use of large quantity of organic
solvent, the presence of which is considered to be
toxic and detrimental to the environment.

This is why one of the aims of the present
invention is to provide a process which makes it
20 possible to obtain a stable dispersion of
(poly)isocyanates in water.

Another aim of the present invention is to
provide a monomer which permits (poly)isocyanate
formulations in aqueous phase, with a view to
25 responding to the progress in the techniques and
regulations which tend to make the organic solvents
disappear.

In order to solve this problem, there is

already a description of the preparation of aqueous emulsions of oils, especially of high viscosity, by separate introduction in two different steps [sic] of two types of amphiphilic surface-active agents (which
5 have different "HLB" values when this scale can be employed) into a conventional mixing apparatus.

However, these techniques are expensive in respect of energies and difficult to use. They demand mixing devices capable of giving high shears.

10 This is why one of the aims of the present invention is to provide a process which makes it possible to employ equipment which does not give high shears.

Another aim of the present invention is to
15 provide a process which avoids high consumptions of energies.

Another aim of the present invention is to provide a process which makes it possible to obtain a narrow particle size distribution of particularly fine
20 droplets.

The Applicant Company has found a process for the preparation of aqueous emulsions of viscous phases based on preferably viscous, advantageously masked (poly)isocyanate oils and/or gums and/or resins, using
25 a conventional mixing apparatus and not requiring the obligatory use of two types of surface-active agents.

Such a process makes it possible to prepare emulsions of advantageously masked (poly)isocyanate

oils and/or gums and/or resins of completely controlled and relatively homogeneous particle size.

The process forming the subject of the invention is characterized in that a mixture consisting
5 of the following is blended

- 100 parts by weight of an advantageously masked (poly)isocyanate(s) phase (A) of dynamic viscosity at 25°C which is at least equal to 3 Pa s, preferably at least equal to 30 Pa s. Or [sic] of
10 consistency at 25°C which does not exceed 2000, advantageously masked (poly)isocyanate(s) phase including at least one oil and/or at least one gum and/or at least one resin:

- 2 to 20 parts by weight, preferably from 3 to
15 15 parts by weight of water;

-- 2 to 20 parts by weight, preferably from 3 to 15 parts by weight of at one least surface-active agent (B) or a combination of 0.5 to 10 parts by weight, preferably of 1 to 10 parts by weight of at least one
20 surface-active agent (B) and of 2.5×10^{-4} to 20 parts by weight, preferably of 0.001 to 15 parts by weight of at least one thickening water-soluble polymer (C) of molecular mass higher than 10 000 g/mole, preferably higher than 100 000 g/mole,

25 the said surface-active agent or mixture of surface-active agents exhibiting an HLB of at least 10 and the relative quantities of water and of constituent(s) (B) and optionally (C) being such that

the viscosity or the consistency of the mixture of water + surface-active agent(s) + optional thickening water-soluble polymer(s) is close to or higher than one tenth of the viscosity or consistency of the

5 advantageously masked (poly)isocyanate(s) phase (A), preferably close to or higher than the viscosity or consistency of the advantageously masked (poly)isocyanate(s) phase (A);

the said blending being carried out over a

10 period and in shearing conditions which are sufficient to obtain an emulsion of "oil-in-water" type of particle size of the order of 0.1 to 5 micrometres, preferably of the order of 0.2 to 3 micrometres;

in that the mixture is then optionally

15 diluted with water as a function of the desired solids content.

According to the invention a small scatter is obtained with a $d_{90} - d_{10}$ which is at most equal to 4, more generally to 1.5 micrometres, preferably to

20 1 micrometre.

For a good implementation of the invention the dynamic viscosity measurements are preferably carried out at 25°C with the aid of a Brookfield viscometer according to AFNOR standard NFT 76 102 of

25 February 1972; the determination of the consistency may be performed by measuring the penetrability with the aid of a penetrometer, for example according to one of the standards AFNOR NFT 60 119, NFT 60 123, NFT 66 004,

ASTM D 217, D 937, D 1321 and D 5.

As examples of advantageously masked (poly)isocyanate(s) (A) which can be used there may be mentioned those consisting of:

5 - polymethylene diisocyanates (generally ω, ω'), it being possible for the chain sequencing of the methylenes to be interrupted by an aromatic nucleus or by an oxygen,

 - the compounds originating from these
10 derivatives to obtain a biuret, a dimer or a trimer.

 - it is appropriate to cite the prepolymer(s) of these products, which are formed by the reaction of isocyanate functional group(s) with a diol in proportions which define the number of the
15 prepolycondensate units and ensures [sic] that virtually all of the end functional groups are isocyanates.

 It is also possible to cite the compounds of addition of the above derivatives to polyols which have
20 at least 3 alcohol functional groups.

 The isocyanate functional groups are advantageously masked (this term is preferable to that of "blocked", frequently employed in texts of Anglo-American sources or those culturally adapted thereto,
25 and this for two reasons the isocyanate functional group has actually reacted so that it are no longer at all isocyanate and when they are "released" there is no certainty in any case that one passes through an

isocyanate intermediate, secondly this masking is not absolute since properties similar to the isocyanate are gradually encountered again at certain temperature).

[sic]

5 According to one of the most surprising methods of the present invention, it has been possible to demonstrate that the emulsion technique employed makes it possible to obtain stable emulsions of unmasked (poly)isocyanate(s).

10 The relative chemical instability of the isocyanates in the presence of phases containing water molecules not only has not prevented the formation of the emulsion whose physical stability is remarkable, but also appears to have been significantly reduced by
15 the emulsification. It appears, to an extent which depends especially on the dilution, on the surface-active agents and on the emulsifiers, that the emulsion technique protects the (poly)isocyanates for a while from chemical decomposition.

20 Thus the advantageously masked (poly)isocyanate(s) may advantageously correspond to the following formula:



25 where A denotes an organic backbone which has n free valencies, p being between 2 and 7 (closed interval) advantageously between 2 and 4 (closed interval);

 where NCOblock denotes an isocyanate

functional group which is advantageously masked (or protected) or otherwise.

It is appropriate to mention that the total number of carbons of the said monomer is advantageously
5 between 10 and 100, preferably between 20 and 100, more preferably between 25 and 75.

The backbone A may be made up from a heavy polyamine (including anilines) which, for example, has a carbon number equal to at least 6 advantageously to
10 10, preferably to 15 [which is converted into isocyanate by the action of phosgene in a manner which is per se known].

The backbone A may also be that of the trimers and of the biurets.

15 Among the masking groups it is possible to choose groups containing mobile hydrogen whose pKa is at most equal to 14, advantageously to 12 preferably to 10 more preferably 8.

The higher the pKa, the more it is desirable
20 that the masking agent should be volatile.

The masking agents are chosen so that the emulsion should be stable at its storage temperature.

Among the chemical functional groups capable of masking isocyanates, the following functional groups
25 may be mentioned by way of examples, or rather of paradigm:

- alcohols and thiols
- oximes

- hydroxylamines
- acids
- amides and imides
- betadiketones
- 5 - pyrazoles

The advantageously masked (poly)isocyanate(s) phase (A) may advantageously be chosen from the phases of the list hereinafter:

- An oil and/or a gum and/or a resin
- 10 containing a (poly)isocyanate group of viscosity of at least 3 Pa s, preferably of the order of 30 to 2,500 Pa s. Or [sic] of consistency of the order of 200 to 2,000.

- A mixture of oil(s) and/or gum(s) and/or
- 15 resin(s) containing a (poly)isocyanate group, mixture of viscosity at least equal to 3 Pa s, preferably of the order of 30 to 2,500 Pa s. Or [sic] of consistency of the order of 200 to 2,000.

- A mixture of oil(s) and/or gum(s) and/or
- 20 resin(s) containing advantageously masked (poly)isocyanate groups and of at least one solvent (or diluent) for the said oil and/or gum and/or resin, mixture of viscosity at least equal to 3 Pa s, preferably of the order of 30 to 2,500 Pa s. Or [sic]
- 25 of consistency of the order of 200 to 2,000.

The surface-active agents (B) used may be nonionic of HLB higher than 10, preferably of the order of 10 to 20, anionic, cationic, zwitterionic or

amphoteric of HLB higher than 10.

The nonionic surface-active agents may be chosen from alkoxylated fatty acids, polyalkoxylated alkylphenols, polyalkoxylated fatty alcohols, 5 polyalkoxylated or polyglycerolated fatty amides, polyglycerolated alcohols and aliphadiols, ethylene oxide-propylene oxide block polymers etc. As well as alkylglucosides, alkylpolyglucosides, sugar ethers, sugar esters, sugar glycerides, sorbitan esters, etc. 10 And the ethoxylated compounds of these sugar derivatives exhibiting an HLB of at least 10. [sic]

The anionic surface-active agents may be chosen from alkali metal alkylbenzenesulphonates, monoalkyl sulphates, alkyl ether sulphates, alkylaryl 15 ether sulphates, dialkylsulphosuccinates, alkyl phosphates, ether phosphates, etc., exhibiting an HLB of at least 10.

Among the cationic surface-active agents there may be mentioned aliphatic or aromatic fatty 20 amines, aliphatic fatty amides, quaternary ammonium derivatives, etc. exhibiting an HLB of at least 10.

Among the zwitterionic or amphoteric surface-active agents there may be mentioned betaines and their derivatives, sultaines and their derivatives, 25 lecithins, imidazoline derivatives, glycines and their derivatives, amidopropionates, fatty amine oxides, etc. exhibiting an HLB of at least 10.

The thickening polymers (C) are soluble in

water to at least 50 %; examples of thickening polymers which may be mentioned are:

- Those obtained by chemical synthesis, such as polyvinyl alcohols, polyethylene glycols,
5 polyvinylpyrrolidones, alkali metal polyacrylates etc.

- Those extracted from plants and optionally modified, such as carrageenates, alginates, methyl celluloses, hydroxypropyl celluloses, hydroxyethyl celluloses etc.

10 The relative quantities of water, of surface-active agent(s) and of optional thickening polymer(s) are functions of the viscosity of the advantageously masked (poly)isocyanate(s) phase including at least one oil and/or one gum and/or one resin containing a
15 (poly)isocyanate group and of the nature of the (mixture of) surfactant(s) and of the nature of the (mixture of) optional thickening polymer(s).

In the absence of thickening polymer the weight ratio of water/water+surface-active agent(s) is,
20 for example, of the order of 20/100 to 70/100, preferably of the order 25/100 to 60/100 so as to stabilize an emulsion of an advantageously masked (poly)isocyanate(s) phase consisting of an oil containing a (poly)isocyanate group of viscosity of the
25 order of 30 Pa s to 500 Pa s, with the aid of a nonylphenol which has 9 or 10 ethoxy units as the only surface-active agent.

The use of an aqueous phase consisting of

water and sodium dodecyl sulphate as the only surface-active agent, in a weight ratio of water/water+surface-active agent of 5/7 and containing from 0.5 to 2 % of its weight of hydroxyethyl cellulose as thickening
5 polymer, allows the stabilization of oils of viscosity of the order of 5 Pa s TO [sic] 30 Pa s.

It is preferable, above all when the isocyanates are not masked, to choose thickening agents and surfactants which are substantially inert towards
10 the isocyanate functional groups under the conditions of manufacture of the emulsion, especially at the temperature at which the emulsion is made, and in the storage conditions.

The operation of emulsifying the
15 advantageously masked (poly)isocyanate(s) phase may be carried out:

- by the introduction of at least one oil and/or one gum and/or at least one resin + optional solvent(s) + optional
20 (poly)isocyanate into a mixture of water + surface-active agent(s) + optional water-soluble polymer(s), the optional filler(s) being present in the aqueous mixture and/or introduced into the said mixture, and then
25 blending at a temperature of the order of 10 to 50°C in mixers of the extruder type with single or multiple screw(s), turbine planet wheel mixers, static mixers, blade, screw and

arm mixers;
- or, preferably, by introduction of water into
an oil(s) and/or gum(s) and/or resin(s)
present in totality or partially [for example
5 50-90 % of the total quantity of oil(s)
and/or gum(s) and/or resin(s)] + optional
solvent(s) + optional filler(s) + surface-
active agent(s) + optional water-soluble
polymer(s) mixture, then blending at a
10 temperature of the order of 10 to 50°C in
mixers of the extruder type with single or
multiple screw(s), turbine planet wheel
mixers, static mixers, blade, screw and arm
mixers etc. The optionally remaining quantity
15 of oil(s) and/or gum(s) and/or resin(s) being
introduced into the mixture after the
formation of the "oil-in-water" emulsion
while the blending is maintained. [sic]
One of the advantages of the present
20 invention lies in the use of equipment developing
relatively low shears, in general at least equal to 10^2
but advantageously at most equal to 10^5 preferably to
 10^4 , more preferably around 10^3 . These reference
measurements are carried out in continuous pure water
25 phase.

The emulsions of advantageously masked
(poly)isocyanate oils and/or gums and/or resins
obtained according to the process of the invention are

particularly stable in storage; they can be very fine and monodisperse; their solids content may range from 25 (or less, depending on the intended application of the said emulsions) to 98 %, it being possible for the
5 adjustment of the solids content to be carried out by dilution.

It is possible to obtain emulsions with organic diluent contents which are as varied as possible; it is thus possible to obtain emulsions
10 containing no organic diluents.

When it is desired to emulsify an unmasked tolonate, it is preferable that the solids content should be as high as possible in general at least higher than 3/4 advantageously than 9/10 preferably
15 than 19/20.

According to the invention it is possible to obtain such emulsions either directly, for example at higher temperature, or by producing an emulsion with organic diluent, an emulsion which will be subsequently
20 treated to evaporate the said organic diluents.

It is obvious that the organic diluents will have been chosen so that they are easily capable of being evaporated in presence of water.

These emulsions may be employed for the
25 preparation of (poly)isocyanate-based compositions in virtually all their uses, etc.

The invention is also aimed at an emulsion of mixtures of the (poly)isocyanate(s) with the compounds

which must be polycondensed with it, this being especially when the (poly)isocyanate(s) are masked.

In particular, these emulsions may be useful for, and usable in, paints.

5 The composition of the paints may also include a coloured base. Consisting of a pigment and of titanium oxide. [sic]

 The aqueous phase advantageously contains soluble oligo- or poly-mers [sic] of polyol or polyol-
10 (poly)amine condensate or polyester-polyol type in sufficient quantity to permit the final polycondensation.

 Either the condensation reactant(s) is liposoluble and in this case the emulsion is produced
15 by introducing the said reactant(s) into the (poly)isocyanates phase (noncontinuous phase) or by emulsifying them separately and mixing the various emulsions in which the continuous phase is the aqueous phase; or the reactant(s) are water-soluble and can,
20 with appropriate surface-active agents, be used as agent for diluting the aqueous phase (continuous phase).

 These are the polyols usually employed during condensations with the common isocyanates.

25 Among the polyols it is possible especially to employ those which are mentioned in European Patent Application published under No. 0358979, especially when the isocyanates are not masked.

When the (poly)isocyanate(s) are masked, either phase may contain a "demasking" catalyst in an appropriate form which is known per se. Thus, according to an embodiment of the invention the composition additionally comprises a catalyst for deblocking the isocyanate functional groups. (cf. Journal of Applied Polymer Science "Catalysis of the Isocyanate - Hydroxyl Reaction" vol. IV, issue No. 11, p. 207, (1960), J.W. Britain).

These catalysts are known in themselves and are advantageously chosen from those which induce a temperature of release of the isocyanate functional groups which is at most equal to the usual temperature of the final operations of setting of the varnish or of the paint or of equivalents.

The release temperature induced by the catalysts is advantageously at least equal to approximately 100°C [sic].

It is appropriate to point out that the protecting groups are released more easily if the nitrogen of the protected isocyanate functional group is bonded to an unsaturated, especially aromatic, carbon, which may sometimes be a drawbacks [sic].

In the coating application it is preferable that the nitrogen of the protected isocyanate functional group should be bonded to a saturated carbon (sp^3 hybridization). In the case where the isocyanates are not masked; [sic] such isocyanates bonded to a

saturated carbon (sp^3 hybridization) resist hydrolysis well especially in the case where the said carbon is secondary and preferably tertiary.

5 The backbone A may also be that of the trimers and of the biurets.

The mean size of the droplets is advantageously between $0.01\ \mu\text{m}$ and $20\ \mu\text{m}$, preferably between $0.1\ \mu\text{m}$ and $10\ \mu\text{m}$.

10 The examples are given by way of indication and cannot be considered as a limit of the field and of the spirit of the invention.

Definition

15 The Tolonate employed here is the product of the trimerization of hexamethylene diisocyanate [lacuna]

The tolodate D2 is the product of the trimerization of hexamethylene diisocyanate advantageously masked with methyl ethyl ketoxime and diluted with an aromatic petroleum fraction [Solvesso 20 100 (registered trademark)] until the latter reaches 25 % by volume.

Example 1:

25 The following are introduced into a closed 250-cm^3 reactor fitted with a scraper blade stirring system (IKA model (registered trademark) [sic]:

2.5 g of Antarox 461 P (registered trademark)

2.5 g of water

The mixture is stirred at 150

revolutions/min⁻¹ [sic] for 5 minutes. A thick paste is formed, with a dynamic viscosity of 780 Pa s at a 1 s⁻¹ shear rate. 85 g of Tolonate D2 (registered trademark), of 4.2 Pa s dynamic viscosity at a shear rate of 1 s⁻¹ [sic] are added over approximately 20 minutes, with constant stirring at approximately 350 revolutions/min⁻¹ [sic].

At the end of the addition of the Tolonate D2 (registered trademark) the mixture is blended with the same stirring so as to reach a limiting particle size.

10 g of water are added.

The emulsion obtained has a solids content of 87.5 % and a particle size, measured with the Sympatec (registered trademark) laser particle size analyser, of 0.6 µm with a d₉₀ - d₁₀ size distribution equal to 0.70 µm.

Example 2:

The operation described above is repeated with, on the one hand:

0.7 g of Antarox 461 P (registered trademark)
0.9 g of water

and, on the other hand, 15 g of methyl ketoxime-blocked [sic] Tolonate (registered trademark) at a concentration of 15 % in Solvesso. This isocyanate has a dynamic viscosity of 57 Pa s at a shear rate of 1 s⁻¹. At the end of the addition of the Tolonate (registered trademark) the emulsion is stirred for about ten minutes and then diluted with water to have a

Tolonate (registered trademark) solids content of 70 %..
The final emulsion has a particle size, measured with
the Sympatec (registered trademark) laser particle size
analyser, of 1.1 μm with a $d_{90} - d_{10}$ size distribution
5 equal to 1.2 μm .

Example 3:

The operation described in Example 1 is
repeated with, on the one hand, the same surface agents
and, on the other hand, the ϵ -caprolactam-blocked
10 Tolonate (registered trademark) at a concentration of
25 % in RPDE of dynamic viscosity 7.2 Pa s at a shear
rate of 1 s^{-1} .

The emulsion is kept stirred for about
fifteen minutes at 350 revolutions/min⁻¹ [sic] to have a
15 mean particle size, measured with Sympatec (registered
trademark) laser particle size analyser, of 0.55 μm
with a $d_{90} - d_{10}$ size distribution equal to 0.75 μm .

Example 4:

The operation described in Example 1 is
20 repeated with, on the one hand, the same surface agents
and, on the other hand, a mixture of hydroxylated [sic]
polyester resin Desmophen 690 (registered trademark)
and of Tolonate D2 (registered trademark) in the mass
ratio of 1:1 which has a 21 Pa s dynamic viscosity at a
25 shear rate of 1 s^{-1} .

The emulsion is kept stirred for about
fifteen minutes at 300 revolutions/min⁻¹ to have a mean
particle size, measured with the Sympatec (registered

trademark) laser particle size analyser, of $1.1 \mu\text{m}$ with a $d_{90} - d_{10}$ size distribution equal to $1.4 \mu\text{m}$.

The final emulsion is diluted with water to have a solids content of 85 %.

5 Example 5:

The following are introduced into a closed 250 cm^3 reactor fitted with a scraper blade stirring system:

2.0 g of TTAB, cationic surfactant

10 3.0 g of water

The mixture is stirred at 150 revolutions/ min^{-1} [sic] for 5 minutes. A thick paste is formed, with a dynamic viscosity of 86 Pa s at a 1 s^{-1} shear rate.

15 80 g of Tolonate D2a (registered trademark), of 5 Pa s dynamic viscosity at a shear rate of 1 s^{-1} , are added over approximately 120 minutes with continuous stirring at approximately 350 revolutions/ min^{-1} . The particle size of the emulsion is
20 measured for each addition of 10 g. The polydispersity of the emulsion is followed so as to obtain a $D_{90}-D_{10}$ [sic] size distribution close to 0.5 (curve).

At the end of the addition of the Tolonate D2a (registered trademark) 10 g of water are added.

25 The emulsion obtained has a solids content of 82 % and a particle size, measured with the Sympatec (registered trademark) laser particle size analyser, of $0.75 \mu\text{m}$ with a $d_{90} - d_{10}$ size distribution equal to

0.95 μm .

Example 6:

The following are introduced into a 200-cm³ beaker with continuous stirring at

5 300 revolution/min⁻¹ [sic]:

4.0 g of sodium dodecyl sulphate, anionic surfactant

4.0 of water [sic].

A thick paste is formed, with a dynamic
10 viscosity of 93 Pa s at a 1 s⁻¹ shear rate, to which
91.5 g of Tolonate D2 (registered trademark) and 2 g of
water are added slowly with the same stirring.

After addition, the stirring is continued for
10 minutes while the proportions of the various
15 constituents are kept constant.

The concentrated emulsion is diluted by
addition of water, still with the same stirring for
5 minutes. The final emulsion has the following
composition: 73 % of Tolonate D2 (registered
20 trademark), 3.2 % of sodium sulphate dodecyl [sic] and
23.8 % of water and a particle size, measured with the
Sympatec (registered trademark) laser particle size
analyser, of 0.97 μm [sic] with a d_{90} - d_{10} size
distribution equal to 1.45 μm .

25 Example 7:

The following are introduced into a closed
250-cm³ reactor fitted with a scraper blade stirring
system (IKA model (registered trademark) [sic]:

2.0 g of TTAB cationic surfactant

3.0 g of water

The mixture is stirred at 150 revolutions/
min⁻¹ [sic] for 5 minutes. A thick paste is formed, with
5 a dynamic viscosity of 86 Pa s at a 1 s⁻¹ shear rate.
85 g of unmasked Tolonate HDT (registered trademark)
are added over approximately 20 minutes with continuous
stirring at approximately 350 revolutions/min⁻¹ [sic].

At the end of the addition of the Tolonate D2
10 [sic] (registered trademark), the mixture is blended
with the same stirring so as to reach a limiting
particle size.

30 g of water are added.

The emulsion obtained has a solids content of
15 87.5 % and a particle size, measured with the Sympatec
(registered trademark) laser particle size analyser, of
0.8 μm with a $d_{90} - d_{10}$ size distribution equal to 1 μm .